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ON THE ELECTROLYSIS OF FUSED METALLIC CHLORIDES.

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ON THE ELECTROLYSIS OF FUSED METALLIC CHLORIDES

by

HUGO JOHN WICHMANN

A Thesis Submitted for the Degree of

MASTER OF ARTS

UNIVERSITY OF WISCONSIN

1907

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ON THE ELECTROLYSIS OF FUSED METALLIC CHLORIDES.

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The only impurity of electrolytic iron as described by Hambüchen and Burgess* is hydrogen. This element is present in the iron when it is taken from the tanks. It has a great influence on the physical properties of the metal, rendering it extremely hard and brittle. In this condition it is useless for ordinary purposes. The best way to get rid of this hydrogen is to heat the metal. The evolution of hydrogen begins at 100° C. and becomes very rapid at a red heat.

Prof. Kahlenberg suggested to me the possibility of obtaining pure electrolytic iron, and other high melting metals, by the electrolysis of electrolytes that contain no hydrogen whatever. If hydrogen does not enter into the composition of either solute or solvent, it cannot enter into the metal as an impurity. This requirement prohibits the use of water or organic solvents, but leaves open the entire field of fused salts.

An enormous amount of work has been done on the electrolytic production of sodium, potassium, lithium, calcium, magnesium, barium, and aluminum from their fused salts. A larger amount of work has also been done by

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*Transactions of the American Electrochemical Society; 1904, page 201.

Richard Lorenz* and his assistants on the electrolysis of fused halogen salts of zinc, cadmium, lead, and silver. On looking over the literature on the subject, I find that but little has been done on the production of high melting metals such as iron, chromium, manganese, copper, silver, nickel, cobalt, and others from their fused salts. Of these, chromium, manganese and copper, seem to be the only ones that have been tried. A few patents have been taken out for the electrolytic production of manganese, chromium or ferro-alloys from fused salts. From the fact that these processes are not in actual use to any great extent, it may be argued that they are not of much practical value. Of course it is well known since the time of Farady that fused silver chloride may be electrolyzed with the production of crystalline silver at the cathode. Th. W. Richards and W. N. Stull** determined the validity of Farady's Law in the case of fused silver nitrate with a degree of accuracy of 1:10000. A little work has also been done on the precipitation of copper from its fused salts. Next to nothing can be found in the literature on the electrolytic precipitation of iron, cobalt, and nickel from fused salts. It was with a desire to obtain a few of these metals from their fused salts that this work was undertaken.

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* Monographien über Angewandte Electrochemie; vols. 21-22.

**Proceedings American Academy of Arts and Science; 38, 409, 1902.
Zeitschrift f. Physikalishe Chemie; 42, 621, 1903.

Only two metals, iron and copper, were taken up for study. Of the iron salts, the chlorides fuse readily and yield electrolytes. The other salts decompose before melting, or melt at too high a temperature. Ferrous chloride in the fused state oxidizes too readily to serve as an electrolyte. Though free from this disadvantage, ferric chloride is very volatile and in addition possesses a strong affinity for water. According to St. Claire Deville* anhydrous ferric chloride and sodium chloride when fused together produce a very limpid, black, rather stable compound, melting at about 200° C. Anhydrous ferric chloride cannot be exposed to the air without atracting moisture and becoming yellow in a few minutes. Clouds of ferric chloride are volatilized even at low temperatures. Pure, fused ferric chloride would be an exceedingly unsatisfactory electrolyte to use. Fusion with sodium chloride diminishes the volatility, on the one hand, and the affinity for water on the other. I have exposed this double chloride to the atmosphere of the laboratory for days, with the formation of only a crust of hydrated ferric chloride on the surface. This electrolyte seemed favorable for electrolysis and was used for the experiment on iron.

A little more work has been done on the electrolysis

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* Comptes Rendus; Vol. 43, 970.

of fused copper salts. Of such salts, the most interesting, from the standpoint of Farady's Law, is cuprous chloride. Buff* electrolyzed fused cuprous chloride in series with a copper voltameter and found approximately twice as much copper corroded from the anode as was deposited on the cathode of the voltameter. He could not determine the increase in weight of the cathode, because of the dentrite formation of the copper. F. Quincke** repeated these experiments of Buff with greater care. He passed a current through a silver and a copper voltameter, and then through fused cuprous chloride into which dipped spiral copper wire electrodes. To remove the frozen cuprous chloride from the electrodes after the electrolysis, he used fused mixtures of sodium and potassium chlorides, dilute hydrochloric acid, or ammonia. I reproduce here a table of his results.

No.	Time	Current	Copper calculated	Cu lost at anode	Cu gained at cathode	Cu found Cu calculated	
						anode	Cathode
1.	30 min.	0.6001 A.	0.3544	0.6585	0.4681	1.858	1.320
2.	20 "	.4804	.1891	.2810	.0927	1.486	0.490
3.	10 "	.3944	.0776	.1704	.1065	2.195	1.372
4.	10 "	.4572	.0900	.2383	.0100	2.648	0.111

The ~~first~~ fourth column gives the amount of copper as cupric copper

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* Annalen der Chemie; Vol. 110, 257, (1859).

** Wiedemann's Annalen der Physic; 36, 270, (1889).

equivalent to the amount of silver deposited in the voltameter. At the anode the amount of corrosion is about two times the amount of deposition on the voltameter. The electrolytic equivalent of copper cannot be determined from these results. Secondary reactions obscure the strict electrolytic reaction. Quincke found that when the copper wires were immersed in the fused cuprous chloride, they lost weight even when no currect was passed. Crystals of copper were formed on the wires near the surface, after they had been placed in the fusion, He believes these crystals are deposited by a current developed between unequally heated portions of the electrodes. This, in brief, is the extent of the work that has been done on the electrolysis of fused copper compounds, as far as I have been able to determine. The experiments described below are the result of an endeavor to obtain electrolytic iron from the fused chlorides, and further to determine the validity of Farady's Law in the case of fused cuprous chloride.

EXPERIMENTAL PART.

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I first endeavored to obtain a deposit of iron from the fused mixture of sodium and ferric chloride. The first difficulty encountered was that of obtaining a suitable container. Ordinary clay crucibles were attacked by the melt, which gradually soaked through them. Porcelain crucibles were too small, and glass beakers too fragile. An iron pot was finally selected, and filled with the fusion consisting of about equal parts by weight of ferric chloride and sodium chloride. The pot was made the anode, and a revolving cylindrical piece of iron, the cathode. The iron pot was placed over a Bunsen burner and the electrolyte kept molten. Difficulty was experienced in keeping the entire electrolyte molten without supreheating it. When heated too highly, ferric chloride was volatilized, and and soon solid sodium chloride would separate out, necessitating the addition of more ferric chloride. As the ferric chloride always becomes somewhat hydrated during the process of mixing with sodium chloride, fumes of hydrochloric acid are given off upon fusing the mixture. A number of runs were made with this electrolyte using various current-densities, and for various lengths of time. During electrolysis the small

of chlorine was noticed. Only small, crystalline, poorly adhering deposits of iron were obtained. The loss of weight at the anode could, of course, not be determined. The cathode always showed signs of corrosion, and lost in weight, even when a deposit was formed. Many secondary reactions evidently occurred that entirely masked the electrolytic reaction. These difficulties led us to abandon for the present the attempt to obtain electrolytic iron from fused salts, and it was decided to study more in detail the electrolytic behavior of fusions presenting perhaps fewer difficulties. We therefore turned our attention to the electrolysis of fused cuprous salts.

The cuprous salts are of interest from the point of view of Farady's Law, because just twice as much copper ought to be precipitated as from a cupric salt. Thus if the same current were passed through a copper voltameter, and then through fused cuprous chloride, the relative amounts of copper deposited in the two cells ought to be in the ratio of 1 : 2. Both cupric and cuprous chlorides melt and become electrolytic conductors. Fused cuprous chloride is somewhat volatile, but sodium chloride has been found to reduce this tendency just as in the case of ferric chloride. On heating anhydrous cupric chloride it breaks down into cuprous chloride and chlorine. When gram molecular quantities of cupric chloride and sodium

chloride are heated together in a porcelain crucible, they melt readily, but chlorine always escapes, and can be easily detected by the smell or by means of starch potassium iodide paper. Molecular quantities of cupric chloride and sodium chloride were heated together to quiet fusion until no more chlorine escaped, and then allowed to cool. A light brown solid was formed. Some of it was weighed out, dissolved in concentrated nitric acid, the solution diluted, and the amount of chlorine determined. 0.2995 gm. of substance contained 0.1~~8~~373 gm. of chlorine or 45.8%. $CuCl_2.NaCl$ requires 55.1% Chlorine and $CuCl.NaCl$ requires 45%. The last chlorine comes off rather slowly, and it is not advantageous to obtain the cuprous chloride by heating the mixture of cupric and sodium chlorides.

Pure cuprous chloride was prepared according to the method described by Max Rosenfeld*. When gram molecular quantities of copper sulphate and sodium chloride are dissolved in the least amount of water, or a strong solution of cupric chloride is placed in a flask and sulphur dioxide passed into it, cuprous chloride separates out as a white crystalline mass.

$$2CuCl_2 + H_2SO_3 + H_2O = 2CuCl + H_2SO_4 + 2HCl.$$

The cuprous chloride is first washed with water saturated

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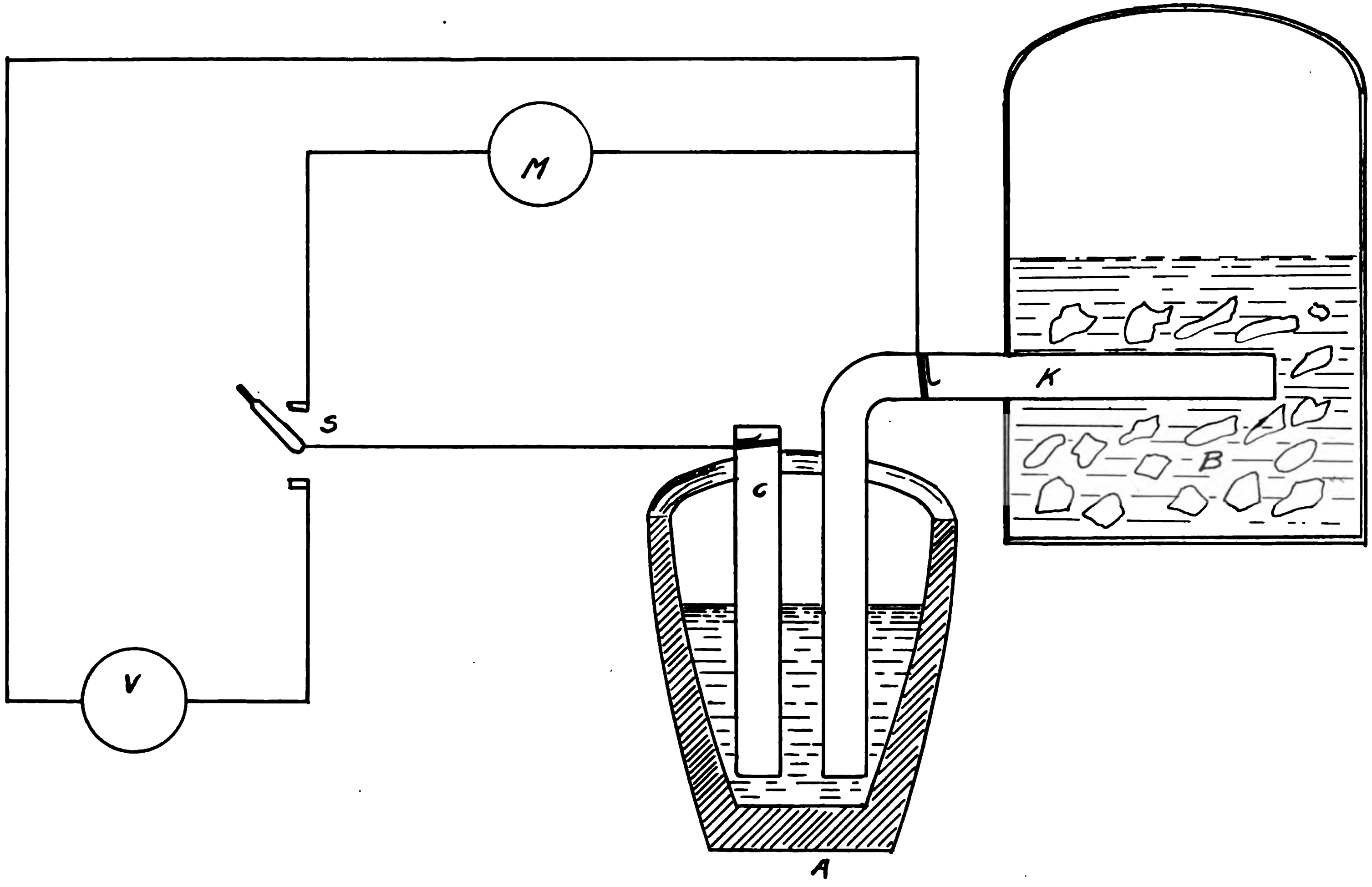
* Berliner Chemische Berichte; (12), 954, (1879).

with sulphur dioxide, upon a Büchner funnel, and then with glacial acetic acid. Cuprous chloride when moist and exposed to the air will rapidly oxidize and turn yellow or green. The pure salt is insoluble in glacial acetic acid, but cupric chloride or oxychloride dissolves. The salt is washed with the glacial acetic acid until the filtrate is colorless, then dried by sucking off the adhering acetic acid on a Büchner funnel, and expelling the remainder of the acid by heating in an air bath. Cuprous chloride made in this manner is finely crystalline, pure white, and stable in the air. This method gives good yields and is easy to follow.

Cuprous chloride melts according to Carnelley at a temperature of 434° C. It volatilizes somewhat readily. Sodium chloride when fused with cuprous chloride lowers the melting point as might be expected from the general behavior of mixed salts. A mixture of one molecule of cuprous chloride to one of sodium chloride melts at a rather high temperature, but one containing three molecules of the former to one of the latter melts at about 300° C. It forms a white crystalline compound. It was used in the following esperiments.

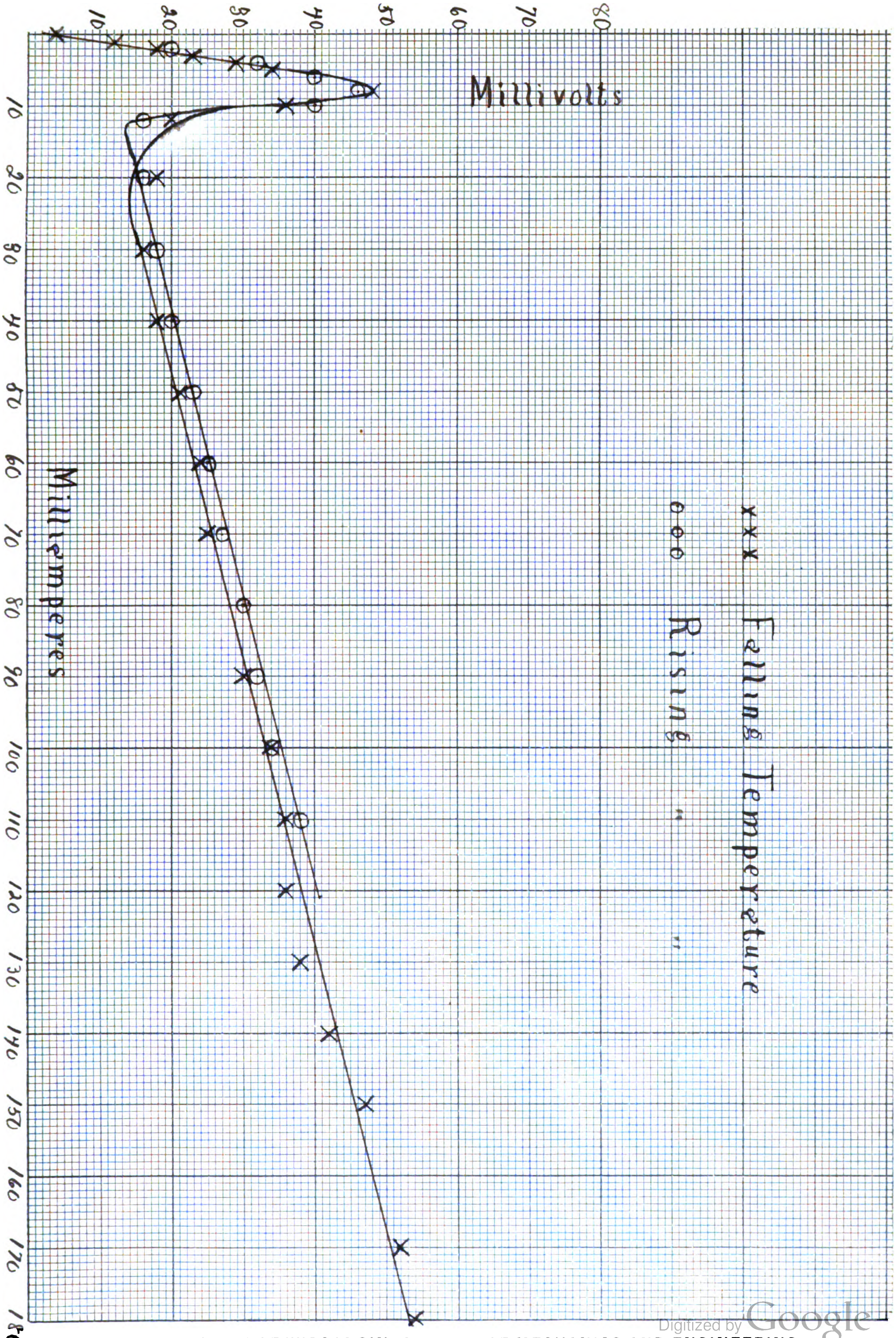
Quincke found that when a copper wire was placed in a bath of fused cuprous chloride, crystals of metallic copper appeared near the top. He ascribed this phenom-

enon to unequal heating. If a strip of copper is placed in an inclined position in the fusion contained in a porcelain crucible, feathery crystals of copperwill appear on the upper side of the strip where the temperature is the lowest. A difference of potential must have existed between the hot bottom part and the relatively colder upper portion, so that a current flowed from the hotter to the colder portion. To test this temperature effect more fully the following experiment was performed. Into the crucible filled with the fusion, a heavy piece of copper wire "K" bent as shown in diagram I, projected and the other end was immersed in a freezing mixture of ice and salt in the vessel "B". Another piece of copper "C" was connected by a fine wire through the switch "S" and the milliammeter "M" to "K". The heavy wire conducting heat away rapidly, was consequently at a lower temperature than "C". Any difference of potential between the two electrodes was read by the millivoltmeter "V". "C" was kept as hot as possible by placing the flame on that side. The apparatus consisted then of two similar electrodes, but kept at different temperatures. A difference of potential was thus set up between them, and a current was observed to flow from one to the other, the difference of potential, and consequently the current , varying with the difference in temperature. As great a difference in the


M
S
V
C
L
K
B
A

temperature of the two electrodes as possible was maintained, and the fusion then allowed to cool, while a series of readings of current and voltage was taken. When the mass was solid, current and difference of potential was zero. Another series of readings was taken with rising temperature.

Falling temperatures		Rising temperatures	
Mili Amp.	Mili Volts	Mili Amp.	Mili Volts.
220	63	2	20
210	60	4	32
200	58	6	40
190	56	8	46
180	54	10	40
170	52	12	16
150	47	20	16
140	42	30	18
130	38	40	20
120	36	50	23
110	36	60	25
100	34	70	27
90	30	80	30
70	25	90	32
60	24	100	34
50	21	110	38
40	18		



UNIVERSITY OF WISCONSIN, COLLEGE OF MECHANICS AND ENGINEERING

30	16
20	18
12	20
10	36
8	48
5	34
4	29
3	23
2	19
1	12
0	4

It is seen that the potential is a direct function of the difference in temperature. The maximum point in the curve indicates the melting point. There is a sudden dip in electromotive force when the substance melts probably due to equalization of temperature. We have here a thermo electric battery. The hot electrode corresponds to the zinc plate of an ordinary galvanic cell, and the cold electrode to the copper or carbon plate. The current passes from the hot to the cold copper electrode in the electrolyte and in the opposite direction in the external circuit. It appears somewhat remarkable that such considerable currents as I have found should be produced in this manner between electrodes indetical in composition. I have connected such a couple in series with a copper

voltameter and in this manner measured the magnitude of the current produced. When the cold rod is taken out, and the adhering salt removed by hydrochloric acid, a mass of copper is found adhering to it. It does not adhere well, readily coming off on rubbing with the finger.

Various investigators have observed these thermo-electric forces. Their discovery is ascribed to Th. Andrews.* He found that differences of potential existed between two pieces of platinum immersed in a bead of borax or sodium carbonate provided one is hotter than the other. Gladstone and Tribe** observed that crystals of silver appeared on one of two rods of silver connected externally and immersed in fused silver chloride. They found electromotive forces of 0.02 volts, the current passing from the hot to the cold rod through the electrolyte. L. Poincare*** determined the thermo electromotive force obtained by immersing two similar electrodes at unequal temperatures in the same molten salt. He determined that the electromotive force developed is proportional to the temperature difference of the electrodes and not to their absolute temperature. Andrews, working with different fused salts, observed after a time, reversals of the direction of the current as the salts are heated up. I found no

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* Pogg. Ann. d. Phys. 41, 164, (1837).
Phil. Mag. (3), 10, 433, (1837).

** Phil. Mag. (5), 11, 508, (1881).

*** Ann. de Chem. et de Phys. (6), 21, 338, (1890).

such effect, the current always going in one direction, namely from the hot electrode through the electrolyte to the cold electrode.

The deposit of copper obtained at the cathode in the electrolysis of the fused chlorides, was always crystalline, feathery, and loosely adherent. The nature of the deposit was not affected by varying current densities. To obtain quantitative results, two difficulties must be overcome. 1st. The temperature must be maintained uniform throughout the cell, to prevent the formation of thermo-electric couples. These couples, occuring on the same electrode or between parts of the two electrodes, could not affect the quantitative results, provided the copper be precipitated in a dense, adherent form. Such is not the case. If the electrolysis is carried out in a crucible heated by a Bunsen burner, nodules of non-adhering copper appear on the electrodes. Local high current densities, must occur and prevent an adherant deposition of copper.

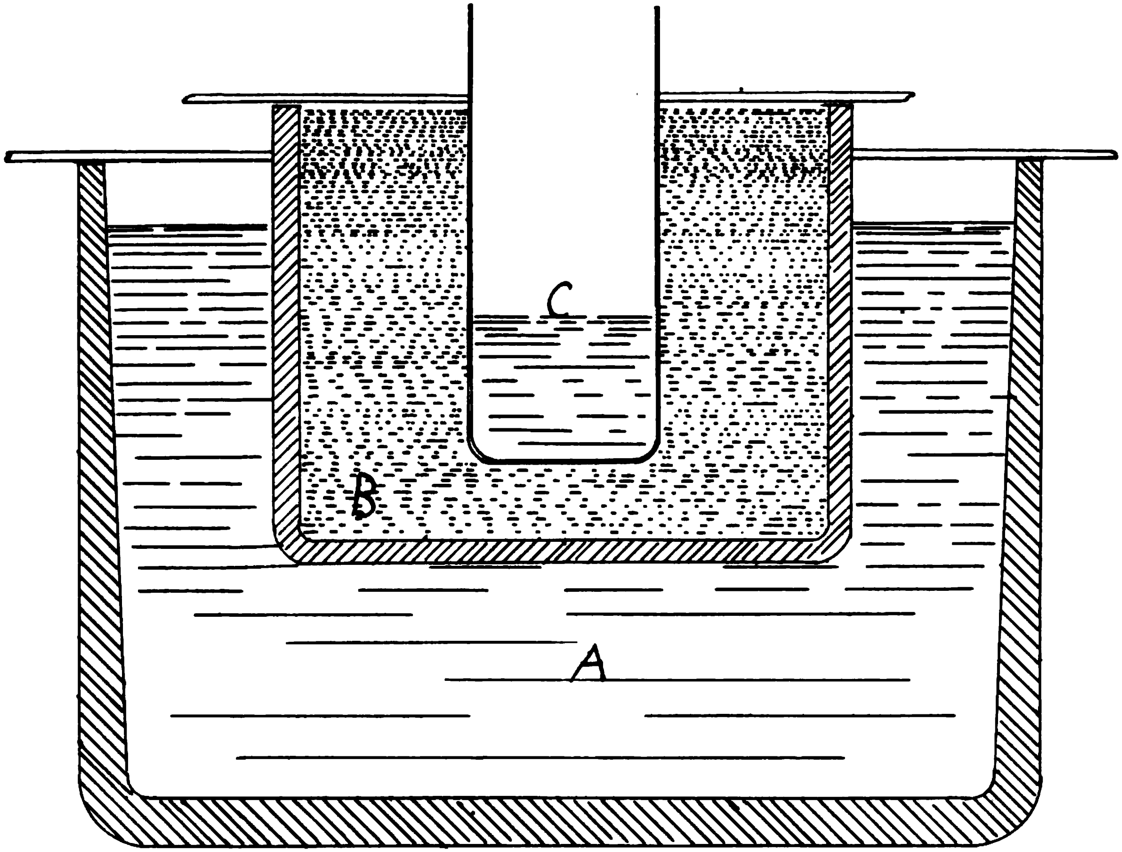
2nd. A feathery deposition of copper must be prevented. The copper must be deposited on the cathode in such a form that it can be washed and weighed. To accomplish this, use was made of the well known principle of electro-deposition upon a rotating cathode. A good deposition of metal can often be obtained on a rotating

cathode, when it is impossible to get one on a stationary cathode.

Considerable difficulty was experienced in devising a suitable apparatus. No clay crucible would hold the electrolyte. Glass beakers and porcelain crucibles are liable to break on cooling. Metal vessels like iron would be useless, because the copper would be precipitated on the iron. Copper, silver, or platinum vessels are corroded, besides presenting the danger of short circuits. Glass beakers were finally used, a new one being needed for each run. In order to get a uniform temperature, these beakers were immersed in a bath of molten tin. This was not very satisfactory. The beaker had to be removed from the bath after each experiment, for if left in the molten bath it invariably cracked which entailed the loss of the fusion. To avoid this, porcelain crucibles were placed in iron crucibles and the latter immersed in the bath. Still the crucibles were liable to crack on alternately cooling and heating. Although the tin had a low specific heat and would be expected to heat the contents of the crucible evenly, I found that this was not the case, since I always found loosely adhering deposits on the anode, plainly due to the uneven heating. Finally the apparatus shown in Fig.II was constructed. "A" is an iron vessel filled with melted tin, and heated by burners underneath.

A cast-iron vessel "B" formed by cutting away the upper part of a mercury container is forced down into the bath. This vessel is filled with fine sand. The glass beaker "C" containing the electrolyte is placed in "B" and surrounded by the sand. In the first experiment a 150 cc. beaker was used, and immersed up to the rim in the sand. Later a talled beaker was used. The electrolyte was fused at the bottom of the beaker. The sand in "B" prevented too rapid heating of the electrolyte, but when the temperature was once high enough for fussion it remained there a long time. When one considers that the electrolyte was well surrounded by the hot sand and by a molten bath, and that it was, moreover, vigorously stirred, it would appear that the temperature must be as nearly uniform in all parts of the electrolyte as is possible to get it. Still when a milli-voltmeter was attached to the two electrodes it was found that small differences of potential did exist. This was probably due to the heat conducted away by the stirring rod attached to the cathode.

The electrodes themselves were constructed as shown in the accompanying photographs.. The anode was bent so as to fit the sides of the beaker, and thus prevent its striking the cathode. A narrow strip extended up the sides of the beaker by which electrical contact was made. The cathode was a hollow cylindrical piece of copper, thraded


C
B
A

near the top. It was screwed into an iron cap which was attached to a rotating apparatus, run by a motor. The cathode was 4.5 cm. long and 1.5 cm. in diameter. When immersed 2 cm. in the electrolyte it offered about 10 sq. cm. surface. The anode was about 2 cm. in height, and extended half way around the sides of the beaker.

A current, measured by the amount of silver deposited in a voltameter was then passed through the system. From the weight of the silver deposited, the theoretical amount of copper calculated as cuprous copper can be computed. The weight of silver bears to the copper the ratio of 107.9 : 63.6. The electrodes, after a run, were placed in a warm, concentrated solution of sodium chloride for a few minutes until the adhering cuprous chloride had dissolved, then washed with water and alcohol and dried.

If the fusion be stirred with a glass rod between stationary electrodes, the copper always separates out in feathery, often fern-like growths. The rotating rod can easily brush off these deposits, and render the results useless. But if the cathode itself be rotated, at a fairly rapid rate, and the current density is not too high, this feathery deposit can be suppressed. The deposit is then composed of small bright red crystals clinging to the cathode with a considerable degree of tenacity. After

washing and drying, they can be removed by vigorous rubbing. The anode corrosion is peculiar. It is not even, but shows a pitted surface. The form of the electrodes and their appearance after use can be seen in the accompanying photograph.

In the manner described, the following results were obtained.

No.	Am't of Ag	Current	Time	Copper calculated	Loss at anode	Gain at cathode
1.	0.8930 gm.	0.6 A.	22 min.	0.5263	0.9672	0.1568
2.	1.0640 "	1.5-1.7	10 "	.6271	.6508	.1740
3.	0.7077 "	0.8-0.9	12 "	.4171	.4420	.3478
4.	.3336 "	0.5	10 "	.1966	.7217	-.1178
5.	.3922 "	0.5	12 "	.2311	.4925	-.0176
6.	.3100 "	0.4-0.5	10 "	.1827	.3752	-----
7.	.5524 "	0.4-0.7	12 "	.3256	.3840	.3010
8.	.4876 "	0.6	10 "	.2874	.4010	.2298
9.	.4632 "	0.5-0.6	10 "	.2730	.3618	.2154

Experiments 1 and 2 were conducted in a glass beaker, enclosed in a copper vessel, surrounded by asbestos, and the whole immersed directly in the molten tin bath. Considerable deposits, due to couples, were formed on the anode. In No. 2 a high current density was employed. While the anode corrosion seems to accord with Farady's Law, the cathode deposit was poor. The deposit was powdery and very loosely adherent. It is seen from the very first that

the results are not strictly in accord with Farady's Law. The loosely adherent copper deposited by the thermo-currents doubtless account for the discrepancies. In the later experiments, the thermal effects were largely suppressed, only relatively small thermo-electromotive forces being detected, varying between 0 and 15 millivolts. In experiments 4 and 5 small anodes were used. They were simply strips of copper about 1 cm. wide and immersed to about 2 cm. in the electrolyte. I found in these cases, that the cathode lost instead of gaining weight. It had a very pitted appearance, that looked at first sight like a deposit. There was evidently corrosion going on, that was not electrolytic . No concentration effects can possibly be present, and the thermal effects had been largely overcome. It was noticed, however, that, after the fusion had solidified, there were always three layers. A thin skin of black substance on the top, then a layer of white cuprous-sodium chloride, and at the bottom a black layer. This lowest layer was examined with a lense. It was plainly seen that it was not homogeneous. Hydrochloric acid dissolved it without evolution of gas. Nitric acid slowly dissolved it, a gas being given off that liberated iodine from potassium iodide. The piece so treated became white. Cuprous chloride reduces nitric acid with the formation of nitrous acid or nitric oxide. On warming with concentrated nitric

acid, the brown fumes of nitrogen peroxide could be plainly seen. On warming the sample in sodium chloride solution, a black residue always remains that is soluble in hydrochloric acid. This black substance at the bottom of the melt, is a mixture of cuprous chloride and cupric oxide. At the high temperature prevailing the cuprous chloride is oxidized on being stirred in contact with the air, and liberates chlorine. This chlorine then attacks the copper electrodes as fast as it is formed. The cupric oxide formed at the same time sinks to the bottom on account of its greater specific gravity. This doubtless accounts for the non-electrolytic corrosion of the electrodes.

The experiments were now varied, in that a rapid current of carbon dioxide was conducted into the beaker containing the electrolyte during electrolysis. A taller beaker than formerly was employed, and was covered by a layer of asbestos. The arrangement can be best seen from the photograph. Numbers 7, 8, and 9 present the results obtained by this method. Although leaving much to be desired in point of accuracy, they conform to Farady's Law much better than the former results. Lack of time prevented me from performing the experiment in an atmosphere entirely devoid of oxygen. Although the carbon dioxide was passed in rapidly, currents of air might still find ingress. To prove Farady's Law in the case of molten

cuprous chloride, the experiments would have to be performed in an inert atmosphere, and in such a way that the action of thermo-couples are suppressed. The latter difficulty can be overcome but to avoid the oxidation of the electrolyte is more difficult in view of the necessity of rotating the cathode. The decomposition of the fusion, in the presence of air also probably accounts for the poor results obtained in the case of the experiments on iron. To obtain good results, therefore, in the electrolysis of chlorides of high melting metals a low temperature, rapid rotation of cathode, and an inert atmosphere are essential factors. The metals always have a tendency to separate out in a crystalline form which can only be overcome by rapid rotation. Probably thick deposits can never be obtained.

In the case of low melting metals the practice of adding alkali chloride gives good results, as is shown by the work of Lorenz on the electrolysis of zinc and lead chlorides. The lowering of the melting point by addition of sodium chloride ought to be especially useful in the electrolysis of cadmium chloride. The boiling point of cadmium is between the melting point and boiling point of cadmium chloride. Here the phenomenon of the "metallic mist" is especially pronounced. By adding sodium chloride the melting point could be lowered to near

the melting point of cadmium, and thus lessen the vapor pressure of the cadmium. The same could be said of the chlorides of bismuth, antimony, zinc, tin and lead. If the salts contain water, hydrochloric acid is always formed on fusion. Cupric, ferric, nickel and cobalt chlorides give off chlorine on melting with sodium chloride in test tubes. Of these cobalt chloride gives off its chlorine only at a high heat, and in very small amounts. Nickel chloride has a great tendency to volatilize. The deposition of these metals would probably present the same difficulties as found in the case of copper, especially those that give off chlorine on simply heating. As these metals can be produced better and far more efficiently in other ways, it would hardly be profitable to spend much time on the electrolysis of ~~thier~~ their salts in the fused state.

Although the results have been somewhat disappointing from the quantitative standpoint, yet the difficulties have been overcome to a sufficient extent to demonstrate that Farady's Law is valid for cuprous chloride in the fused state. Experiments 3, 7, 8, and 9 show clearly that the amount corroded or deposited is far more than corresponds to a cupric salt.

SUMMARY.

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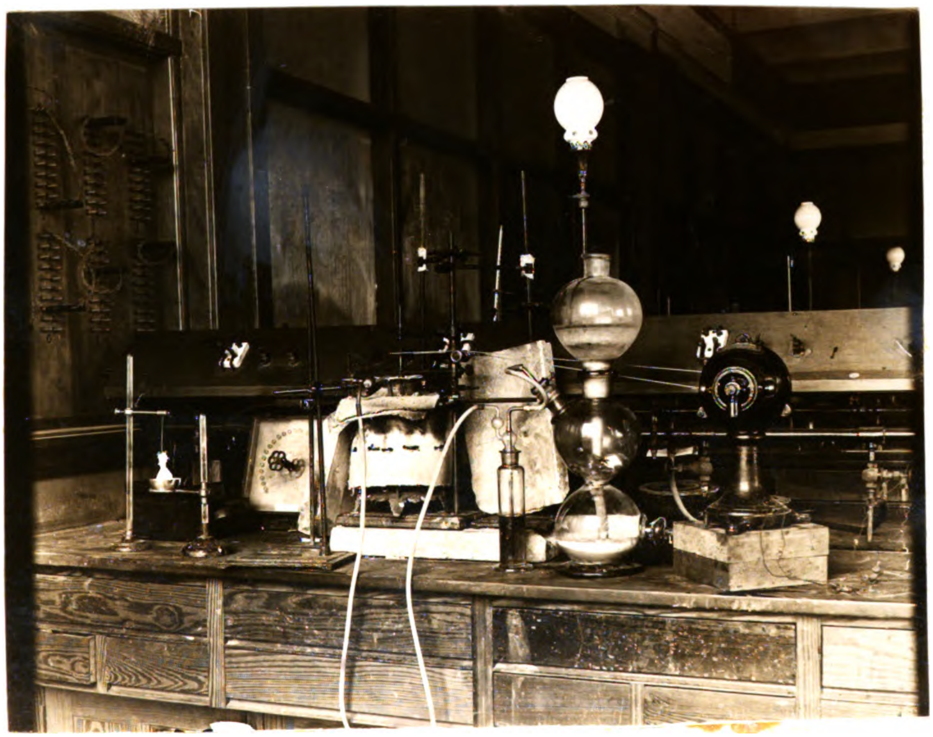
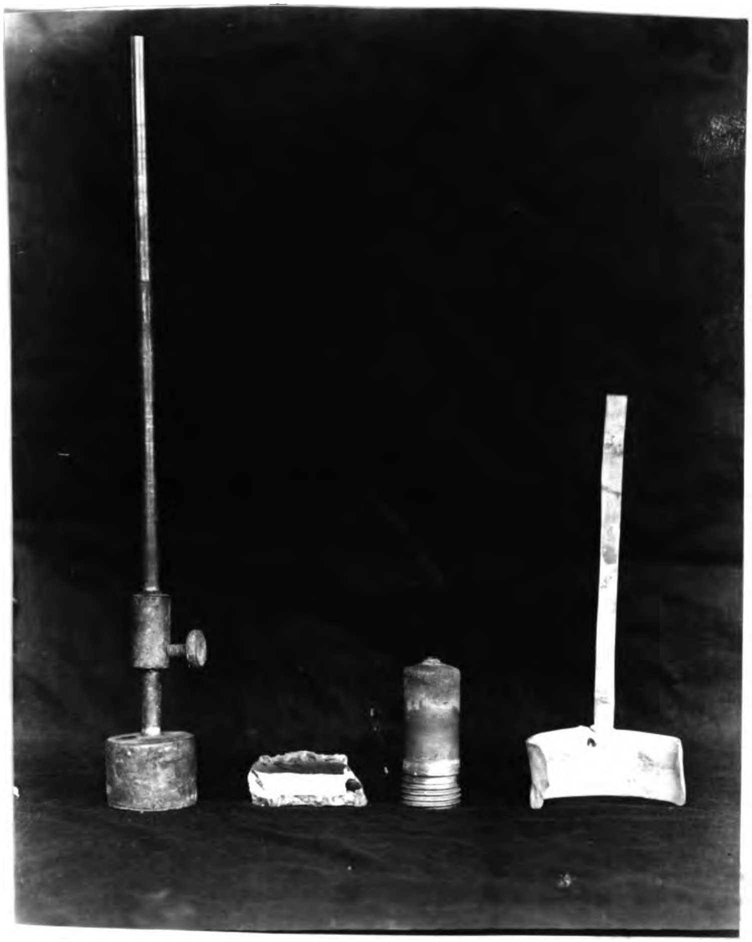
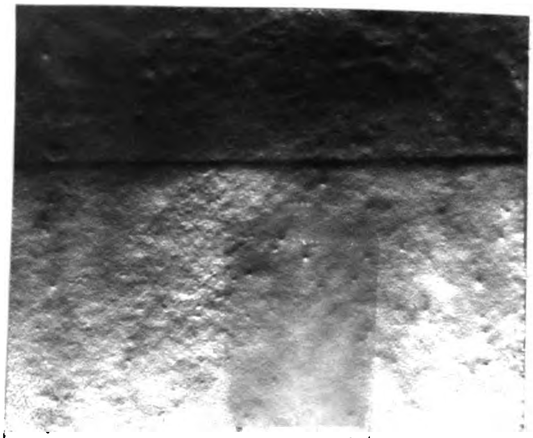
The results of these experiments may be briefly summarized as follows. Ferric chloride can be fused with sodium chloride, to form a compound that is far more stable at 200° C. than ferric chloride itself. This fusion however, does not give good electrolytic deposits of iron. Further, cuprous chloride fused with sodium chloride gives a fusion that melts at 300° C. Copper deposited from this electrolyte is feathery in form unless the cathode is rotated. If the electrodes are not at a uniform temperature considerable thermo-currents may be developed that precipitate non-adhering copper on the colder parts. A method has been shown whereby these currents may be suppressed. Results according to Farady's Law are not possible in the air due to the oxidation of the cuprous chloride. Finally, a method has been indicated for the suppression of these secondary reactions.

In conclusion, I take this opportunity of paying my acknowledgements to Prof. Kahlenberg who suggested and under whose supervision these experiments were carried out.







Approved L. Kahlenberg

June 8, 1907.

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